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Dated 19 September 2003

Patents Form 1/77

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1/77

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P01/7700 0.00-0225554.5

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The Patent Office

Cardiff Road
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NP10 8QQ

1. Your reference

PPD 70142/GB/P

2. Patent application number
(The Patent Office will fill in this part)

01 NOV 2002

0225554.5

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

SYNGENTA Participations AG
Schwarzwaldallee 215
CH-4058 Basel
SWITZERLAND

Patents ADP number *(if you know it)*

If the applicant is a corporate body, give the country/state of its incorporation

SWITZERLAND

8290835001

4. Title of the invention

CHEMICAL COMPOUNDS

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Martin Keith Osborn
Intellectual Property Department
Syngenta Limited
Jealott's Hill International Research Centre
PO Box 3538
Bracknell, Berkshire, RG42 6YA
UNITED KINGDOM

Patents ADP number *(if you know it)*

8019945001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*
—	

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
See note (d))

YES (b)

Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	
Description	36
Claim(s)	03
Abstract	00
Drawing(s)	00

10. If you are also filing any of the following, state how many against each item.

Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	
Request for preliminary examination and search *(Patents Form 9/77)*	
Request for substantive examination *(Patents Form 10/77)*	
Any other documents *(please specify)*	

11. I/We request the grant of a patent on the basis of this application.

Syngenta Participations AG

Signature Joanna Carmen Chandler Date 31/10/02

Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

Joanna Carmen CHANDLER = 01344 414365

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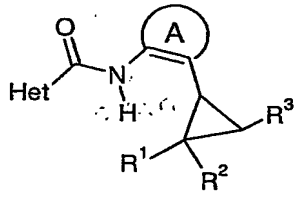
CHEMICAL COMPOUNDS

The present invention relates to novel ortho-cyclopropyl-thienyl-carboxamides which have microbiocidal activity, in particular fungicidal activity. The invention also relates to the preparation of these compounds, to novel intermediates used in the preparation of these compounds, to preparation of these novel intermediates, to agrochemical compositions which comprise at least one of the novel compounds as active ingredient, to the preparation of the compositions mentioned and to the use of the active ingredients or compositions in agriculture or horticulture for controlling or preventing infestation of plants by phytopathogenic microorganisms, preferably fungi.

The present invention provides a compound of formula (I):



(I)

where

Het is a 5- or 6-membered heterocyclic ring containing one to three heteroatoms, each independently selected from oxygen, nitrogen and sulphur, provided that the ring is not 1,2,3-triazole, the ring being substituted by groups R^4, R^5 and R^6;

A is a thienyl ring (selected from all possible thienyl isomers) being substituted by groups R^7 and R^8;

R^1 and R^2 are each, independently, hydrogen, halo or methyl;

R^3 is optionally substituted C_{2-12} alkyl, optionally substituted C_{2-12} alkenyl, optionally substituted C_{2-12} alkynyl, optionally substituted C_{3-12} cycloalkyl, optionally substituted phenyl or optionally substituted heterocyclyl;

R^4, R^5 and R^6 are each, independently, selected from hydrogen, halo, cyano, nitro, C_{1-4} alkyl, C_{1-4} haloalkyl, C_{1-4} alkoxy(C_{1-4})alkylene and C_{1-4} haloalkoxy(C_{1-4})alkylene, provided that at least one of R^4, R^5 and R^6 is not hydrogen; and

R^7 and R^8 are each, independently, hydrogen, halogen, C_{1-4}alkyl or C_{1-4} haloalkyl.

Halo is fluoro, chloro or bromo.

Each alkyl moiety is a straight or branched chain and is, for example, methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, iso-propyl, n-butyl, sec-butyl, iso-butyl, tert-butyl or neo-pentyl. Likewise, each alkylene moiety is a straight or branched chain.

When present, each optional substituent on an alkyl moiety is, independently, selected from halo, hydroxy, cyano, $COOC_{1-4}$alkyl, formyl, nitro, C_{1-4}alkoxy, C_{1-4} haloalkoxy, C_{1-4} alkylthio, C_{1-4} haloalkylthio, HC(OR')=N and R'R''NN=C(H); where R' and R'' are, independently, hydrogen or C_{1-4} alkyl.

Alkenyl and alkynyl moieties can be in the form of straight or branched chains. The alkenyl moieties, where appropriate, can be of either the (E)- or (Z)-configuration. Examples are vinyl, allyl and propargyl.

When present, each optional substituent on alkenyl or on alkynyl is, independently, selected from those optional substituents given above for an alkyl moiety.

Cycloalkyl includes cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

When present, each optional substituent on cycloalkyl is, independently, selected from C_{1-3} alkyl and those optional substituents given above for an alkyl moiety.

The term heterocyclyl refers to a non-aromatic or aromatic ring containing up to 10 atoms including one or more (preferably one or two) heteroatoms selected, each independently, from O, S and N. Examples of such rings include 1,3-dioxolanyl, tetrahydrofuranyl, morpholinyl, thienyl and furyl.

When present, each optional substituent on phenyl or on heterocyclyl is, independently, selected from C_{1-6} alkyl and those optional substituents given above for an alkyl moiety. When present, there are up to four optional substituents on phenyl, each independently selected.

It is preferred that, when present, each optional substituent on an alkyl moiety is, independently, selected from halo, hydroxy, methoxy, trifluoromethoxy, difluoromethoxy, cyano and nitro.

It is preferred that, when present, each optional substituent on alkenyl or on alkynyl is, independently, selected from halo and cyano.

It is preferred that, when present, each optional substituent on cycloalkyl is, independently, selected from methyl, ethyl, trifluoromethyl, methoxy, trifluoromethoxy and cyano.

It is preferred that, when present, each optional substituent on phenyl or on a heterocyclyl group is, independently, selected from halo, hydroxy, methoxy, trifluoromethoxy, difluoromethoxy and cyano.

It is preferred that Het is pyrrolyl, pyrazolyl, thiazolyl, pyridinyl, pyrimidinyl, thiophenyl, furyl, isothiazolyl or isoxazolyl (more preferably pyrrolyl, pyrazolyl or thiazolyl), each being substituted by groups R^4, R^5 and R^6.

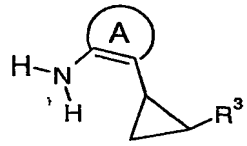
Preferably R^1 and R^2 are, independently, hydrogen or fluoro.

Preferably R^3 is C_{2-6} alkyl, optionally substituted C_{3-8} cycloalkyl, phenyl, thienyl or furyl.

Preferably R^4, R^5 and R^6 are, independently, selected from hydrogen, halogen, C_{1-4} alkyl, C_{1-4} haloalkyl and C_{1-4} alkoxy(C_{1-4})alkylene, provided that at least one of R^4, R^5 and R^6 is not hydrogen. More preferably R^4, R^5 and R^6 are, independently, selected from hydrogen, halogen, methyl, C_{1-2} haloalkyl and methoxymethylene, provided that at least one of R^4, R^5 and R^6 is not hydrogen.

Preferably R^7 and R^8 are, independently, selected from hydrogen, halogen and methyl

Compounds of formula (II):



(II)

where A is an unsubstituted thienyl ring (selected from all possible thienyl isomers) and R^3 is as defined above for a compound of formula (I), are also novel and are useful as intermediates in the preparation of compounds of formula (I).

Therefore, in another aspect the present invention provides a compound of formula (II), where A is an unsubstituted thienyl ring (selected from all possible thienyl isomers) and R^3 is as defined above for a compound of formula (I).

The compounds of formulae (I) and (II) may exist as different geometric or optical isomers or in different tautomeric forms. For each formula, this invention covers all such isomers and tautomers and mixtures thereof in all proportions as well as isotopic forms such as deuterated compounds.

The compounds in Tables 1 to 18 below illustrate compounds of the invention.

Table V represents Table 1 (when V is 1), Table 2 (when V is 2) and represents Table 3 (when V is 3).

Table W represents Table 4 (when W is 4), represents Table 5 (when W is 5), represents Table 6 (when W is 6), represents Table 7 (when W is 7), represents Table 8 (when W is 8) and represents Table 9 (when W is 9).

Table X represents Table 10 (when X is 10), represents Table 11 (when X is 11) and represents Table 12 (when X is 12).

Table Y represents Table 13 (when Y is 13), represents Table 14 (when Y is 14) and represents Table 15 (when Y is 15).

Table Z represents Table 16 (when Z is 16), represents Table 17 (when Z is 17) and represents Table 18 (when Z is 18).

Table V

Compound Number	R^3
V.1	CH_2CH_3
V.2	$CH_2CH_2CH_3$
V.3	$CH(CH_3)_2$
V.4	$CH_2CH_2CH_2CH_3$
V.5	$CH_2CH(CH_3)_2$
V.6	$C(CH_3)_3$
V.7	$CH_2CH_2CH_2CH_2CH_3$
V.8	$CH_2CH_2CH(CH_3)_2$
V.9	$CH_2CH_2CH(CH_3)_2$
V.10	cyclopropyl
V.11	cyclobutyl
V.12	cyclopentyl
V.13	cyclohexyl
V.14	cycloheptyl
V.15	cyclooctyl
V.16	phenyl

V.17	4-Cl-C_6H_4
V.18	4-F-C_6H_4
V.19	4-Br-C_6H_4
V.20	2-thienyl
V.21	3-thienyl
V.22	2-furyl
V.23	3-furyl
V.24	α-methylcyclopropyl

Table W

Compound Number	R^1	R^2	R^3	R^4	R^5	R^6
W.1	H	H	CH_2CH_3	CF_3	CH_3	H
W.2	H	H	CH_2CH_3	CF_3	CH_2OCH_3	H
W.3	H	H	$CH_2CH_2CH_3$	CF_3	CH_3	H
W.4	H	H	$CH_2CH_2CH_3$	CF_2H	CH_3	H
W.5	H	H	$CH(CH_3)_2$	CF_3	CH_3	H
W.6	H	H	$CH(CH_3)_2$	CF_2H	CH_3	H
W.7	H	H	$CH(CH_3)_2$	CFH_2	CH_3	H
W.8	H	H	$CH(CH_3)_2$	CH_3	CH_3	Cl
W.9	H	H	$CH(CH_3)_2$	CH_3	CH_2CH_3	Cl
W.10	H	H	$CH(CH_3)_2$	CH_3	CH_3	F
W.11	H	H	$CH(CH_3)_2$	CH_3	CH_2CH_3	F
W.12	H	H	$CH(CH_3)_2$	CF_2Cl	CH_3	F
W.13	H	H	$CH_2CH_2CH_2CH_3$	CF_3	CH_3	H
W.14	H	H	$CH_2CH_2CH_2CH_3$	CF_2H	CH_3	H
W.15	H	H	$CH_2CH_2CH_2CH_3$	CH_3	CH_3	F
W.16	H	H	$CH_2CH_2CH_2CH_3$	CH_3	CH_3	Cl
W.17	H	H	$CH_2CH(CH_3)_2$	CF_3	CH_3	H

Compound Number	R^1	R^2	R^3	R^4	R^5	R^6
W.18	H	H	$CH_2CH(CH_3)_2$	CF_2H	CH_3	H
W.19	H	H	$CH_2CH(CH_3)_2$	CFH_2	CH_3	H
W.20	H	H	$CH_2CH(CH_3)_2$	CF_3	CH_2OCH_3	H
W.21	H	H	$CH_2CH(CH_3)_2$	CH_3	CH_3	F
W.22	H	H	$CH_2CH(CH_3)_2$	CH_3	CH_3	Cl
W.23	H	H	$C(CH_3)_3$	CF_3	CH_3	H
W.24	H	H	$C(CH_3)_3$	CF_2H	CH_3	H
W.25	H	H	$C(CH_3)_3$	CF_2H	CH_3	H
W.26	H	H	$C(CH_3)_3$	CH_3	CH_3	F
W.27	H	H	$C(CH_3)_3$	CH_3	CH_3	Cl
W.28	H	H	$C(CH_3)_3$	CF_2Cl	CH_3	H
W.29	H	H	$CH_2CH_2CH_2CH_2CH_3$	CF_3	CH_3	H
W.30	H	H	$CH_2CH_2CH(CH_3)_2$	CF_3	CH_3	H
W.31	H	H	$CH_2CH_2CH(CH_3)_2$	CF_2H	CH_3	H
W.32	H	H	$CH_2CH_2CH_2CH_2CH_2CH_3$	CF_3	CH_3	H
W.33	H	H	cyclopropyl	CF_3	CH_3	H
W.34	H	H	cyclopropyl	CF_2H	CH_3	H
W.35	H	H	cyclopropyl	CH_3	CH_3	F
W.36	H	H	cyclopropyl	CH_3	CH_3	Cl
W.37	H	H	cyclobutyl	CF_3	CH_3	H
W.38	H	H	cyclobutyl	CF_2H	CH_3	H
W.39	H	H	cyclopentyl	CF_3	CH_3	H
W.40	H	H	cyclopentyl	CF_2H	CH_3	H
W.41	H	H	cyclopentyl	CFH_2	CH_3	H
W.42	H	H	cyclopentyl	CF_2Cl	CH_3	H
W.43	H	H	cyclopentyl	CH_3	CH_3	F
W.44	H	H	cyclopentyl	CH_3	CH_3	Cl

Compound Number	R^1	R^2	R^3	R^4	R^5	R^6
W.45	H	H	cyclopentyl	CF_3	CH_3	H
W.46	H	H	cyclopentyl	CF_2H	CH_3	H
W.47	H	H	cyclopentyl	CFH_2	CH_3	H
W.48	H	H	cyclopentyl	CF_2Cl	CH_3	H
W.49	F	F	cyclopentyl	CF_3	CH_3	H
W.50	H	H	cyclopentyl	CH_3	CH_3	F
W.51	H	H	cyclopentyl	CH_3	CH_3	Cl
W.52	H	H	cyclopentyl	CF_3	CH_3	H
W.53	H	H	cyclopentyl	CF_3	CH_2CH_3	H
W.54	H	H	cyclopentyl	CF_2H	CH_3	H
W.55	H	H	cyclopentyl	CFH_2	CH_3	H
W.56	H	H	cyclopentyl	CF_2Cl	CH_3	F
W.57	H	H	cyclopentyl	CH_3	CH_3	F
W.58	H	H	cyclopentyl	CH_3	CH_3	Cl
W.59	H	H	cyclopentyl	CF_3	CH_3	H
W.60	H	H	cyclopentyl	CF_2H	CH_3	H
W.61	H	H	phenyl	CF_3	CH_3	H
W.62	H	H	phenyl	CF_2H	CH_3	H
W.63	H	H	phenyl	CFH_2	CH_3	H
W.64	H	H	phenyl	CH_3	CH_3	F
W.65	H	H	phenyl	CH_3	CH_3	Cl
W.66	H	H	4-F-C_6H_4	CF_3	CH_3	H
W.67	H	H	4-F-C_6H_4	CF_2H	CH_3	H
W.68	H	H	4-Cl-C_6H_4	CF_3	CH_3	H
W.69	H	H	4-Cl-C_6H_4	CF_2H	CH_3	H
W.70	H	H	4-Br-C_6H_4	CF_3	CH_3	H
W.71	H	H	4-Br-C_6H_4	CF_2H	CH_3	H

Compound Number	R^1	R^2	R^3	R^4	R^5	R^6
W.72	H	H	2-thienyl	CF_3	CH_3	H
W.73	H	H	3-thienyl	CF_3	CH_3	H
W.74	H	H	2-furyl	CF_3	CH_3	H
W.75	H	H	2-furyl	CF_3	CH_3	H
W.76	H	H	α-methylcyclopropyl	CF_3	CH_3	H
W.77	H	H	α-methylcyclopropyl	CF_2H	CH_3	H
W.78	H	H	α-methylcyclopropyl	CH_3	CH_3	F
W.79	H	H	α-methylcyclopropyl	CH_3	CH_3	Cl

Table X

Compound Number	R^1	R^2	R^3	R^4	R^5
X.1	H	H	CH_2CH_3	CF_3	CH_3
X.2	H	H	CH_2CH_3	CH_3	CH_3
X.3	H	H	$CH_2CH_2CH_3$	CF_3	CH_3
X.4	H	H	$CH_2CH_2CH_3$	CH_3	CH_3
X.5	H	H	$CH(CH_3)_2$	CF_3	CH_3
X.6	H	H	$CH(CH_3)_2$	CH_3	CH_3
X.7	H	H	$CH(CH_3)_2$	CH_2CH_3	CH_3
X.8	H	H	$CH_2CH_2CH_2CH_3$	CF_3	CH_3
X.9	H	H	$CH_2CH_2CH_2CH_3$	CH_3	CH_3
X.10	H	H	$CH_2CH(CH_3)_2$	CF_3	CH_3
X.11	H	H	$CH_2CH(CH_3)_2$	CH_3	CH_3
X.12	H	H	$C(CH_3)_3$	CF_3	CH_3
X.13	H	H	$CH_2CH_2CH_2CH_2CH_3$	CF_3	CH_3
X.14	H	H	$CH_2CH_2CH_2CH_2CH_3$	CH_3	CH_3
X.15	H	H	$CH_2CH_2CH(CH_3)_2$	CF_3	CH_3

Compound Number	R^1	R^2	R^3	R^4	R^5
X.16	H	H	$CH_2CH_2CH(CH_3)_2$	CH_3	CH_3
X.17	H	H	$CH_2CH_2CH(CH_3)_2$	CH_3	CH_2CH_3
X.18	H	H	$CH_2CH_2CH_2CH_2CH_2CH_3$	CF_3	CH_3
X.19	H	H	$CH_2CH_2CH_2CH_2CH_2CH_3$	CH_3	CH_3
X.20	H	H	cyclopropyl	CF_3	CH_3
X.21	H	H	cyclopropyl	CH_3	CH_3
X.22	H	H	cyclobutyl	CF_3	CH_3
X.23	H	H	cyclobutyl	CH_3	CH_3
X.24	H	H	cyclopentyl	CF_3	CH_3
X.25	H	H	cyclopentyl	CH_3	CH_3
X.26	H	H	cyclopentyl	CF_3	CH_3
X.27	H	H	cyclopentyl	CH_3	CH_3
X.28	F	F	cyclopentyl	CF_3	CH_3
X.29	H	H	cycloheptyl	CF_3	CH_3
X.30	H	H	cycloheptyl	CH_3	CH_3
X.31	H	H	cyclooctyl	CF_3	CH_3
X.32	H	H	cyclooctyl	CH_3	CH_3
X.33	H	H	phenyl	CF_3	CH_3
X.34	H	H	phenyl	CH_3	CH_3
X.35	H	H	4-F-C_6H_4	CF_3	CH_3
X.36	H	H	4-F-C_6H_4	CH_3	CH_3
X.37	H	H	4-Cl-C_6H_4	CF_3	CH_3
X.38	H	H	4-Cl-C_6H_4	CF_3	CH_3
X.39	H	H	4-Br-C_6H_4	CF_3	CH_3
X.40	H	H	4-Br-C_6H_4	CH_3	CH_3
X.41	H	H	2-thienyl	CF_3	CH_3
X.42	H	H	2-thienyl	CH_3	CH_3

Compound Number	R^1	R^2	R^3	R^4	R^5
X.43	H	H	3-thienyl	CF_3	CH_3
X.44	H	H	3-thienyl	CH_3	CH_3
X.45	H	H	2-furyl	CF_3	CH_3
X.46	H	H	2-furyl	CH_3	CH_3
X.47	H	H	3-furyl	CF_3	CH_3
X.48	H	H	3-furyl	CH_3	CH_3
X.49	H	H	α-methylcyclopropyl	CF_3	CH_3
X.50	H	H	α-methylcyclopropyl	CH_3	CH_3

Table Y

Compound Number	R^1	R^2	R^3	R^4
Y.1	H	H	CH_2CH_3	Cl
Y.2	H	H	$CH_2CH_2CH_3$	Cl
Y.3	H	H	$CH_2CH_2CH_3$	Br
Y.4	H	H	$CH_2CH_2CH_3$	CF_3
Y.5	H	H	$CH(CH_3)_2$	Cl
Y.6	H	H	$CH(CH_3)_2$	Br
Y.7	H	H	$CH(CH_3)_2$	CF_3
Y.8	H	H	$CH_2CH_2CH_2CH_3$	Cl
Y.9	H	H	$CH_2CH_2CH_2CH_3$	Br
Y.10	H	H	$CH_2CH_2CH_2CH_3$	CF_3
Y.11	H	H	$C(CH_3)_3$	Cl
Y.12	H	H	$CH_2CH(CH_3)_2$	Cl
Y.13	H	H	$CH_2CH(CH_3)_2$	Br
Y.14	H	H	$CH_2CH(CH_3)_2$	CF_3
Y.15	H	H	$CH_2CH_2CH_2CH_2CH_3$	Cl

Compound Number	R^1	R^2	R^3	R^4
Y.16	H	H	$CH_2CH_2CH_2CH_2CH_3$	Br
Y.17	H	H	$CH_2CH_2CH(CH_3)_2$	Cl
Y.18	H	H	$CH_2CH_2CH(CH_3)_2$	Br
Y.19	H	H	$CH_2CH_2CH_2CH_2CH_2CH_3$	Cl
Y.20	H	H	$CH_2CH_2CH_2CH_2CH_2CH_3$	Br
Y.21	H	H	cyclopropyl	Cl
Y.22	H	H	cyclopropyl	Br
Y.23	H	H	cyclobutyl	Cl
Y.24	H	H	cyclobutyl	Br
Y.25	H	H	cyclopentyl	Cl
Y.26	H	H	cyclopentyl	Br
Y.27	F	F	cyclopentyl	CF_3
Y.28	H	H	cyclohexyl	Cl
Y.29	H	H	cyclohexyl	Br
Y.30	H	H	cyclohexyl	CF_3
Y.31	H	H	cycloheptyl	Cl
Y.32	H	H	cycloheptyl	Br
Y.33	H	H	cycloheptyl	CF_3
Y.34	H	H	cyclooctyl	Cl
Y.35	H	H	phenyl	Cl
Y.36	H	H	phenyl	Br
Y.37	H	H	4-F-C_6H_4	Cl
Y.38	H	H	4-F-C_6H_4	Br
Y.39	H	H	4-F-C_6H_4	CF_3
Y.40	H	H	4-Cl-C_6H_4	Cl
Y.41	H	H	4-Cl-C_6H_4	Br
Y.42	H	H	4-Cl-C_6H_4	CF_3

Compound Number	R^1	R^2	R^3	R^4
Y.43	H	H	4-Br-C_6H_4	Cl
Y.44	H	H	2-thienyl	Cl
Y.45	H	H	2-thienyl	Br
Y.46	H	H	3-thienyl	Cl
Y.47	H	H	3-thienyl	Cl
Y.48	H	H	2-furyl	Cl
Y.49	H	H	2-furyl	Br
Y.50	H	H	3-furyl	Cl
Y.51	H	H	3-furyl	Br
Y.52	H	H	2-pyridyl	Cl
Y.53	H	H	α-methylcyclopropyl	Cl
Y.54	H	H	α-methylcyclopropyl	Br

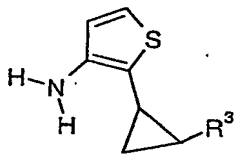
Table Z

Compound Number	R^1	R^2	R^3	R^4
Z.1	H	H	CH_2CH_3	CH_3
Z.2	H	H	$CH_2CH_2CH_3$	CF_3
Z.3	H	H	$CH_2CH_2CH_3$	CH_3
Z.4	H	H	$CH(CH_3)_2$	CF_3
Z.5	H	H	$CH(CH_3)_2$	CH_3
Z.6	H	H	$CH_2CH_2CH_2CH_3$	CF_3
Z.7	H	H	$CH_2CH_2CH_2CH_3$	CH_3
Z.8	H	H	$CH_2CH(CH_3)_2$	CF_3
Z.9	H	H	$CH_2CH(CH_3)_2$	CH_3
Z.10	H	H	$C(CH_3)_3$	CF_3
Z.11	H	H	$C(CH_3)_3$	CH_3

Compound Number	R^1	R^2	R^3	R^4
Z.12	H	H	$CH_2CH_2CH_2CH_2CH_3$	CF_3
Z.13	H	H	$CH_2CH_2CH_2CH_2CH_3$	CH_3
Z.14	H	H	$CH_2CH_2CH(CH_3)_2$	CF_3
Z.15	H	H	$CH_2CH_2CH(CH_3)_2$	CH_3
Z.16	H	H	$CH_2CH_2CH_2CH_2CH_2CH_3$	CF_3
Z.17	H	H	$CH_2CH_2CH_2CH_2CH_2CH_3$	CH_3
Z.18	H	H	cyclopropyl	CF_3
Z.19	H	H	cyclopropyl	CH_3
Z.20	H	H	cyclobutyl	CF_3
Z.21	H	H	cyclobutyl	CH_3
Z.22	H	H	cycloheptyl	CF_3
Z.23	H	H	cycloheptyl	CH_3
Z.24	H	H	cycloheptyl	CF_3
Z.25	H	H	cyclopentyl	CH_3
Z.26	H	H	cyclopentyl	CF_3
Z.27	F	F	cycloheptyl	CH_3
Z.28	H	H	cyclooctyl	CF_3
Z.29	H	H	phenyl	CF_3
Z.30	H	H	phenyl	CH_3
Z.31	H	H	4-F-C_6H_4	CF_3
Z.32	H	H	4-F-C_6H_4	CH_3
Z.33	H	H	4-Cl-C_6H_4	CF_3
Z.34	H	H	4-Cl-C_6H_4	CH_3
Z.35	H	H	4-Br-C_6H_4	CF_3
Z.36	H	H	2-thienyl	CF_3
Z.37	H	H	2-thienyl	CH_3
Z.38	H	H	3-thienyl	CF_3

Compound Number	R^1	R^2	R^3	R^4
Z.39	H	H	3-thienyl	CH_3
Z.40	H	H	2-furyl	CF_3
Z.41	H	H	3-furyl	CF_3
Z.42	H	H	2-pyridyl	CF_3
Z.43	H	H	4-pyridyl	CF_3
Z.44	H	H	α-methylcyclopropyl	CF_3
Z.45	H	H	α-methylcyclopropyl	CH_3

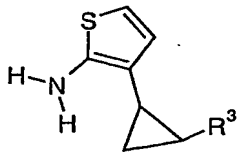
Table 1 provides 24 compounds of formula (IIa)



(IIa)

wherein R^3 is as defined in Table 1.

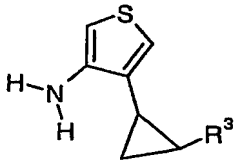
Table 2 provides 24 compounds of formula (IIb)



(IIb)

wherein R^3 is as defined in Table 2.

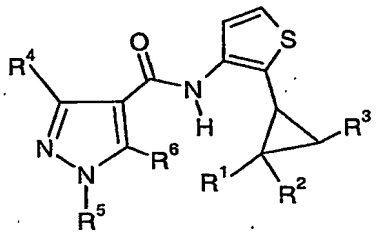
Table 3 provides 24 compounds of formula (IIc)



(IIc)

wherein R^3 is as defined in Table 3.

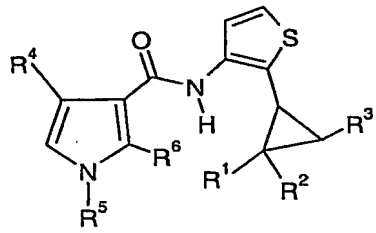
Table 4 provides 79 compounds of formula (Ia):



(Ia)

wherein R^1, R^2, R^3, R^4, R^5 and R^6 are as defined in Table 4.

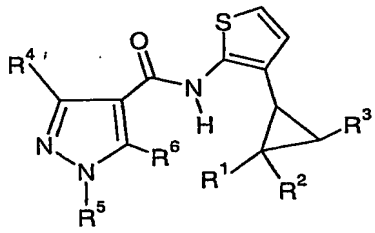
Table 5 provides 79 compounds of formula (Ib):



(Ib)

wherein R^1, R^2, R^3, R^4, R^5 and R^6 are as defined in Table 5.

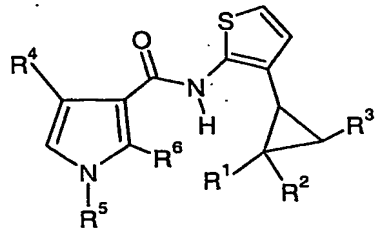
Table 6 provides 79 compounds of formula (Ic):



(Ic)

wherein R^1, R^2, R^3, R^4, R^5 and R^6 are as defined in Table 6.

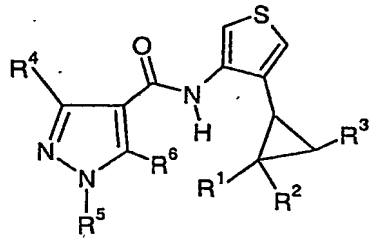
Table 7 provides 79 compounds of formula (Id):



(Id)

wherein R^1, R^2, R^3, R^4, R^5 and R^6 are as defined in Table 7.

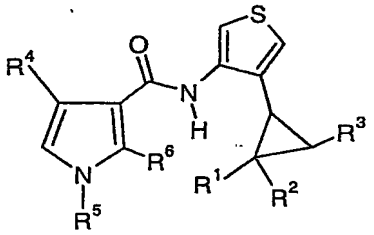
Table 8 provides 79 compounds of formula (Ie):



(Ie)

wherein R^1, R^2, R^3, R^4, R^5 and R^6 are as defined in Table 8.

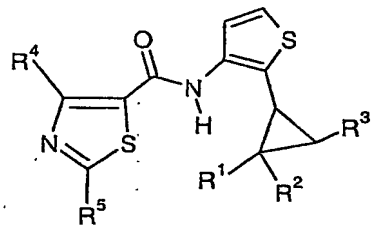
Table 9 provides 79 compounds of formula (If):



(If)

wherein R^1, R^2, R^3, R^4, R^5 and R^6 are as defined in Table 9.

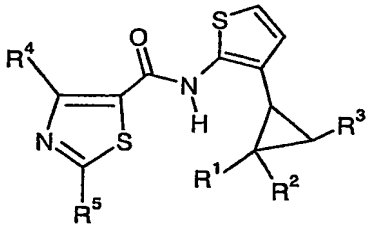
Table 10 provides 50 compounds of formula (Ig):



(Ig)

wherein R^1, R^2, R^3, R^4 and R^5 are as defined in Table 10.

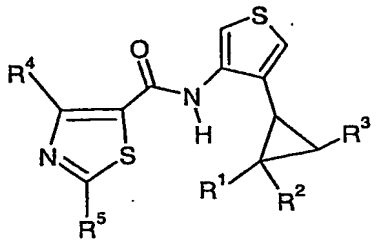
Table 11 provides 50 compounds of formula (Ih):



(Ih)

wherein R^1, R^2, R^3, R^4 and R^5 are as defined in Table 11.

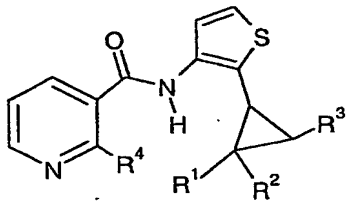
Table 12 provides 50 compounds of formula (Ii):



(Ii)

wherein R^1, R^2, R^3, R^4 and R^5 are as defined in Table 12.

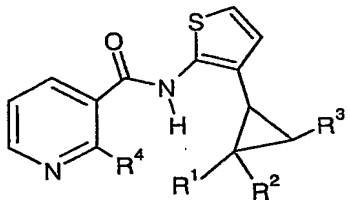
Table 13 provides 54 compounds of formula (Ij):



(Ij)

wherein R^1, R^2, R^3 and R^4 are as defined in Table 13.

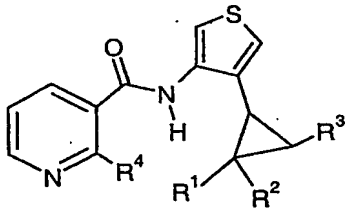
Table 14 provides 54 compounds of formula (Ik):



(Ik)

wherein R^1, R^2, R^3 and R^4 are as defined in Table 14.

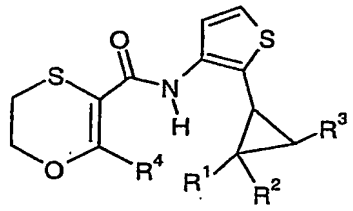
Table 15 provides 54 compounds of formula (IL):



(IL)

wherein R^1, R^2, R^3 and R^4 are as defined in Table 15.

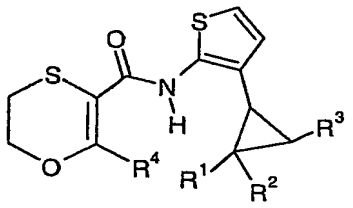
Table 16 provides 45 compounds of formula (Im):



(Im)

wherein R^1, R^2, R^3 and R^4 are as defined in Table 16.

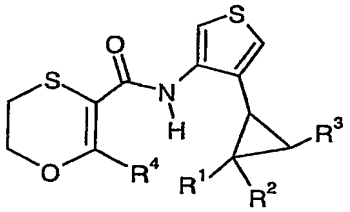
Table 17 provides 45 compounds of formula (In):



(In)

wherein R^1, R^2, R^3 and R^4 are as defined in Table 17.

Table 18 provides 45 compounds of formula (Io):



(Io)

wherein R^1, R^2, R^3 and R^4 are as defined in Table 18.

Throughout this description, temperatures are given in degrees Celsius; "NMR" means nuclear magnetic resonance spectrum; MS stands for mass spectrum; and "%" is percent by weight, unless corresponding concentrations are indicated in other units.

The following abbreviations are used throughout this description:

m.p. =	melting point	b.p.=	boiling point.
s =	singlet	br =	broad
d =	doublet	dd =	doublet of doublets
t =	triplet	q =	quartet
m =	multiplet	ppm =	parts per million

Table 19 shows selected melting point and selected NMR data, all with $CDCl_3$ as the solvent (unless otherwise stated; if a mixture of solvents is present, this is indicated as, for example, ($CDCl_3$ / d_6-DMSO)), (no attempt is made to list all characterising data in all cases) for compounds of Tables 1 to 18. Unless otherwise stated, the data relate to a cis/trans mixture of each compound.

Table 19

Compound Number	^{1}H-NMR data: (ppm/multiplicity/number of Hs).	m.p. / (°C)
1.6	0.67/m/1H; 0.85/m/1H; 0.94/s/9H; 1.03/m/1H; 1.59/m/1H; 3.55/s(broad)/2H(NH_2); 6.52/d/1H; 6.85/d/1H.	oil (trans isomer)
1.10	0.01/m/2H; 0.27/m/2H; 0.58/m/2H; 0.73/m/1H; 0.88/m/1H; 1.31/m/1H; 3.33/s(broad)/2H(NH_2); 6.34/d/1H; 6.68/m/1H.	oil (trans isomer)
1.17	1.35-1.45/m/2H, 1.99/m/1H, 2.12/m/1H, 3.49/s(broad)/2H(NH_2), 6.58/d/1H, 6.93/d/1H, 7.08/d/2H, 7.25/d/2H.	oil (trans isomer)
1.22	0.03/m/4H; 0.49/m/2H; 0.99/s/3H(Me); 1.05/m/1H; 1.23/m/1H; 3.40/s(broad)/2H(NH_2); 6.30/d/1H; 6.62/d/1H.	oil (trans isomer)
4.23		115-116 (trans isomer)
4.24		105-106 (trans isomer)
4.33		103-107
4.34		76-79 (trans isomer)
4.68		147-148 (trans isomer)

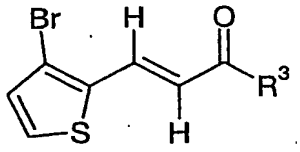
4.69		102-104 (trans isomer)
4.76		100-108
4.77	0.15-0.38/m/8H(cis+trans); 0.60/m/1H(cis); 0.7-0.8 /m/2H(trans); 0.97/s/3H(cis-Me); 1.02/m/1H(cis); 1.19/s/3H(trans-Me); 1.40/m/1H(trans); 1.50/m/1H	resin
	(cis); 1.62/m/1H(trans); 1.98/m/1H(cis); 3.97/s/6H (cis+trans-NMe); 6.88/t/1H(cis-CF_2H) 6.89/t/1H (trans-CF_2H); 7.0/d/1H(trans); 7.06/d/1H(cis); 7.62/d/1H(trans); 7.76/d/1H(cis); 8.03/s/1H(trans); 8.05/s/1H(cis); 8.20/s/1H(trans-NH); 8.38/s/1H(cis-NH).	
4.78		105-113
5.23		90-92 (trans isomer)
5.33		110-112 (trans isomer)
5.76	0.18-0.35/m/8H(cis+trans); 0.58/m/1H(cis); 0.75/m/ 2H(trans); 0.98/s/3H(cis-Me); 1.01/m/1H(cis); 1.18/ s/3H(trans-Me); 1.38/m/1H(trans); 1.47/m/1H(cis); 1.59/m/1H(trans); 1.95/m/1H(cis); 3.70/s/6H(trans+ cis-Nme); 7.00/2xd/2H(trans); 7.08/d/1H(cis); 7.38 /d/1H(trans); 7.40/d/1H(cis); 7.64/d/1H(trans); 7.79 /d/1H(cis); 7.87/s/1H(trans-NH); 8.0/s/1H(cis-NH).	resin
10.12		71-73 (trans isomer)
10.20		93-95 (94% trans)
10.49		85-88

13.11		135-136 (trans isomer)
13.53	0.2-0.35/m/8H(cis+trans); 0.61/m/1H(cis); 0.80/m/2H(trans); 0.99/s/3H(cis-Me); 1.06/m/1H(cis); 1.18/s/3H(trans-Me); 1.40/m/1H(trans); 1.49/m/1H(cis); 1.60/m/1H(trans); 1.99/m/1H(cis); 7.07/d/1H(trans), 7.11/d/1H(cis); 7.42/m/2H(cis+trans); 7.68/d/1H	resin
	(trans); 7.78/d/1H(cis); 8.28/dd/1H(trans); 8.36/m/1H(cis); 8.40/s/1H(trans-NH); 8.53/m/2H(cis+trans); 8.68/s/1H(cis-NH).	

The compounds according to formula (I) may be prepared according to the following reaction schemes.

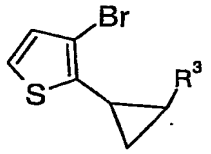
Scheme 1

A compound of formula (IIa) [where R^3 is as defined above for a compound of formula (I)] may be prepared by a reaction sequence starting with a crossed-aldol condensation of 3-bromo-2-formylthiophene with a ketone of formula $CH_3C(O)R^3$ [where R^3 is as defined above for a compound of formula (I)] in the presence of NaOH or KOH in a solvent (such as water or ethanol) and usually under reflux conditions; or alternatively by reaction of 3-bromo-2-formylthiophene with an appropriate Wittig reagent under standard conditions (for example: DMSO, 20°-100°C). The resulting α,β-unsaturated ketone of formula (IIIa) [where R^3 is as defined above for a compound of formula (I)]:



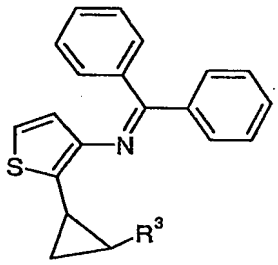
(IIIa)

may then be converted into a compound of formula (IVa) [where R^3 is as defined above for a compound of formula (I)]:



(IVa)

by reacting first with hydrazine hydrate in ethanol under reflux conditions and then heating (in the range 150 to 250^{0}C) in the presence of KOH (distilling off the solvent). After Pd-catalysed [tris-dibenzylidenacetondipalladium; ($Pd_2(dba)_3$) as catalyst] reaction of a compound of formula (IVa) with benzophenonimine in the presence of a strong base [such as Na-tert-butoxide] and a ligand [such as racemic 2,2'-bis(diphenylphosphino)1,1-binaphthyl (BINAP)] in a solvent [for example benzene, toluene or dioxane] at a temperature of 30°C up to reflux temperature, an imine of formula (Va) is obtained [where R^3 is as defined above for a compound of formula (I)]:

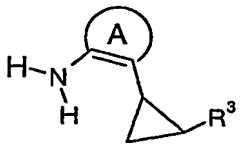


(Va)

After either a transamination reaction of a compound of formula (Va) with hydroxylamine hydrochloride in the presence of a base [such as potassium carbonate or sodium acetate] preferably in MeOH, EtOH or THF and preferably at 20°C-reflux temperature or a hydrolysis reaction of a compound of formula (Va) with an acid [such as HCl or H_2SO_4], a cis/trans-mixture of a compound of formula (IIa) is obtained, which may be further purified by distillation or flash chromatography.

The synthesis of either of the two other possible aminothiophene isomers of formulae (IIb) and (IIc) may be achieved using the methodology described above using an appropriate bromoformylthiophene as starting material.

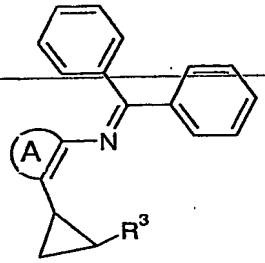
Compounds of formula (II):



(II)

where A is an unsubstituted thienyl ring (selected from all possible thienyl isomers) and R^3 is as defined above for a compound of formula (I), are also novel and are useful as intermediates in the preparation of compounds of formula (I).

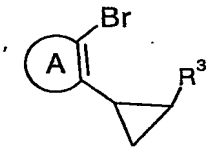
Therefore, in a further aspect the present invention provides a process for preparing a compound of formula (II) from a compound of formula (V)



(V)

where A is an unsubstituted thienyl ring (selected from all possible thienyl isomers) and R^3 is as defined above for a compound of formula (I), comprising either a transamination reaction of a compound of formula (V) with hydroxylamine hydrochloride in the presence of a base or a hydrolysis reaction of a compound of formula (V) with an acid.

Furthermore, in an additional aspect the present invention provides a process for preparing a compound of formula (V) from a compound of formula (IV)



(IV)

where A is a thienyl ring (selected from all possible thienyl isomers) and R^3 is as defined above for a compound of formula (I), comprising tris-dibenzylidenacetondipalladium-catalysed reaction of a compound of formula (IV) with benzophenonimine in the presence of a strong base and a ligand in a solvent at temperatures of 30°C up to reflux temperature.

Scheme 2A

The synthesis of a compound of formula (I) may be accomplished by a CuI-catalysed coupling reaction of an appropriate o-cyclopropylsubstituted bromothiophene precursor with an amide of the type $HetCONH_2$ [where Het is as defined above for a compound of formula (I)] in the presence of an aliphatic diamine [such as 1.2-diamino-cyclohexane], in

the presence of a base [such as potassium carbonate], in a solvent [such as dioxane or toluene] and at a temperature of 50°C up to reflux temperature.

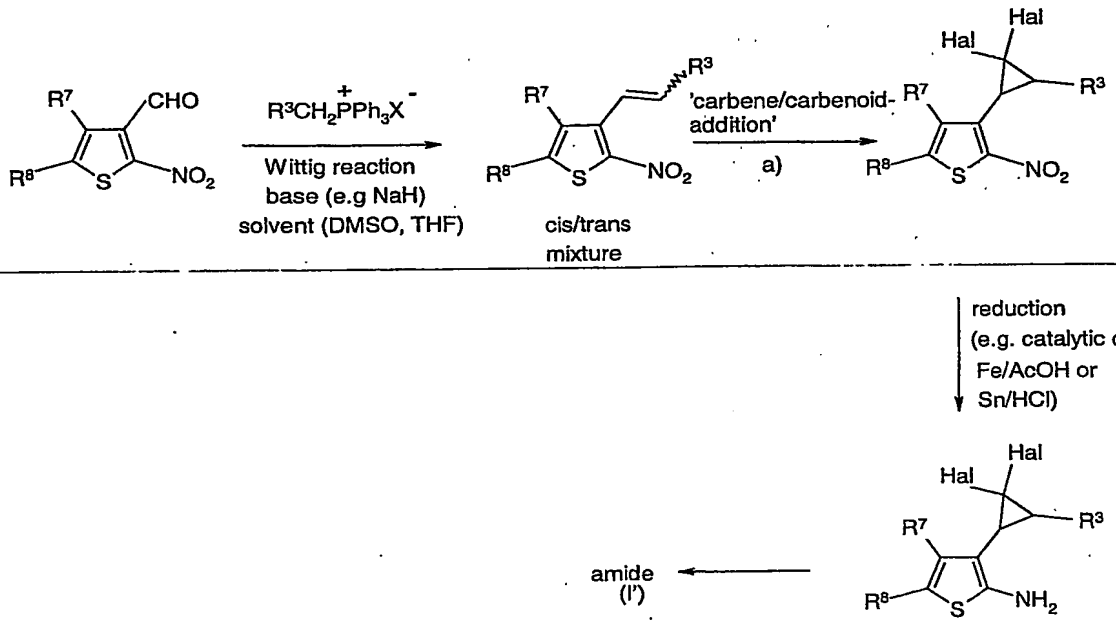
Scheme 2B

A compound of formula (I) may also be prepared by reacting a compound of formula Het-C(=O)-R* [where R* is halogen, hydroxy or C_{1-6}alkoxy, but preferably chloro; and Het is as defined above for a compound of formula (I)] with a compound of formula (IIa), (IIb) or (IIc) as prepared above, in the presence of a base (such as triethylamine, Hunig base, sodium bicarbonate, sodium carbonate, potassium carbonate, pyridine or quinoline, but preferably triethylamine) and in a solvent (such as diethylether, TBME, THF, dichloromethane, chloroform, DMF or NMP) for between 10minutes and 48hours (preferably 12 to 24hours) and between 0°C and reflux (preferably 20 to 25°C). When R* is hydroxy, this is achieved with a coupling agent [such as benzotriazol-1yloxytris(dimethylamino)phosphonium hexafluorophosphate, bis-(2-oxo-3-oxazolidinyl)-phosphinic acid chloride (BOP-Cl), N,N'-dicyclohexylcarbodiimide (DCC) or 1,1'-carbonyl-diimidazole (CDI)].

It will be noted that for the compounds of formula (IIa), (IIb) and (IIc) the only susbstitutuent on the cyclopropyl ring is R^3; in order to prepare, via reactions analagous to scheme 2B, a compound of formula (I) where at least one of R^1 and R^2 is not hydrogen, it is necessary to prepare an appropriate precursor as described in scheme 3.

Scheme 3: Strategies for the synthesis of o-cyclopropylsubst. aminothiophenes where R^1 and R^2 are each, independently, hydrogen, halogen or methyl (provided that R^1 and R^2 are not both hydrogen) and R^7, R^8 are as defined above for a compound of formula(I). The starting material for this series of syntheses is 2-nitrothiophene-3-carboxaldehyde. The synthesis of this 2-nitrothiophene and related copmpounds is described in the literature (for example, Pharmazie 1996, 51, 386, J.Org. Chem. 1989, 54, 5094, Tetr. Letters 1987, 28, 3021 or Chem. Scr. 1980, 15, 20).

Scheme 3A:



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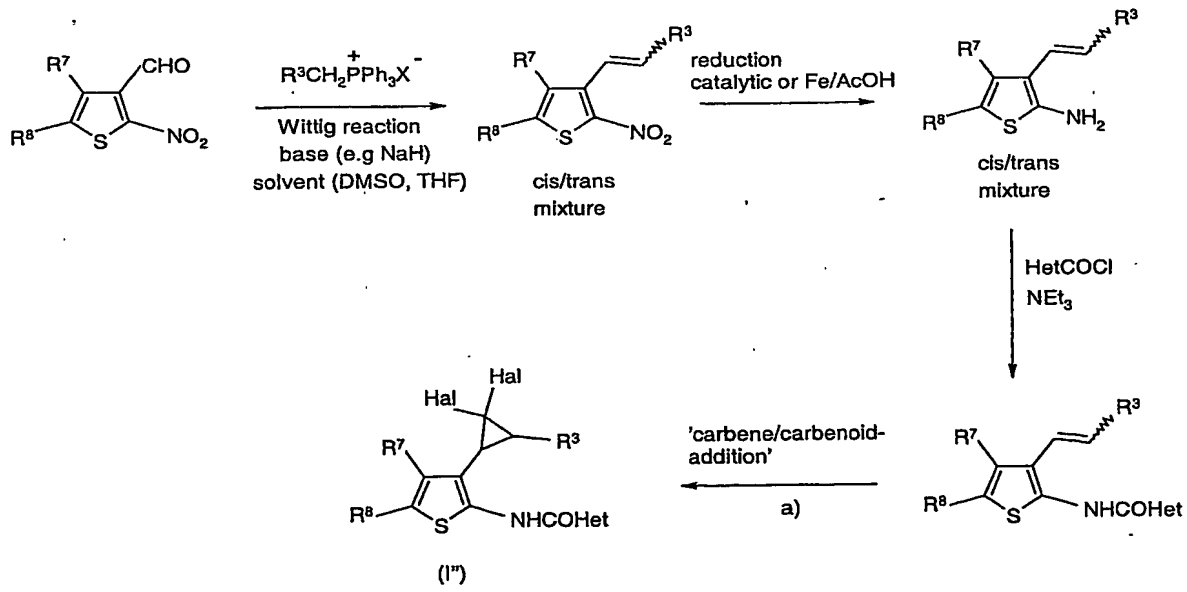
Scheme 3B:



10

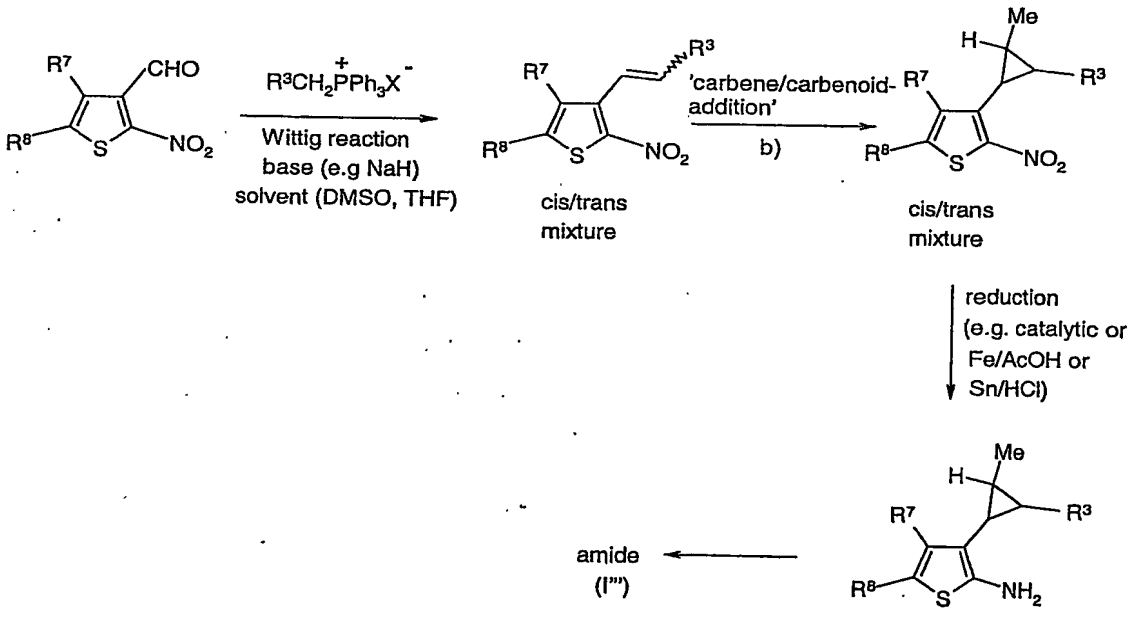
Literature for step a): Hal = Br, Cl, F

a1) (Hal = F): J.Amer.Chem.Soc. 1975, 97, 344, J.Org.Chem. 1990, 55, 5420, J.Chem.Soc. Chem.Comm. 1991, 12, 826, J.Amer. Chem.Soc. 2001,123, 8139 and Russian J. Org.Chem. 2001, 37, 207;

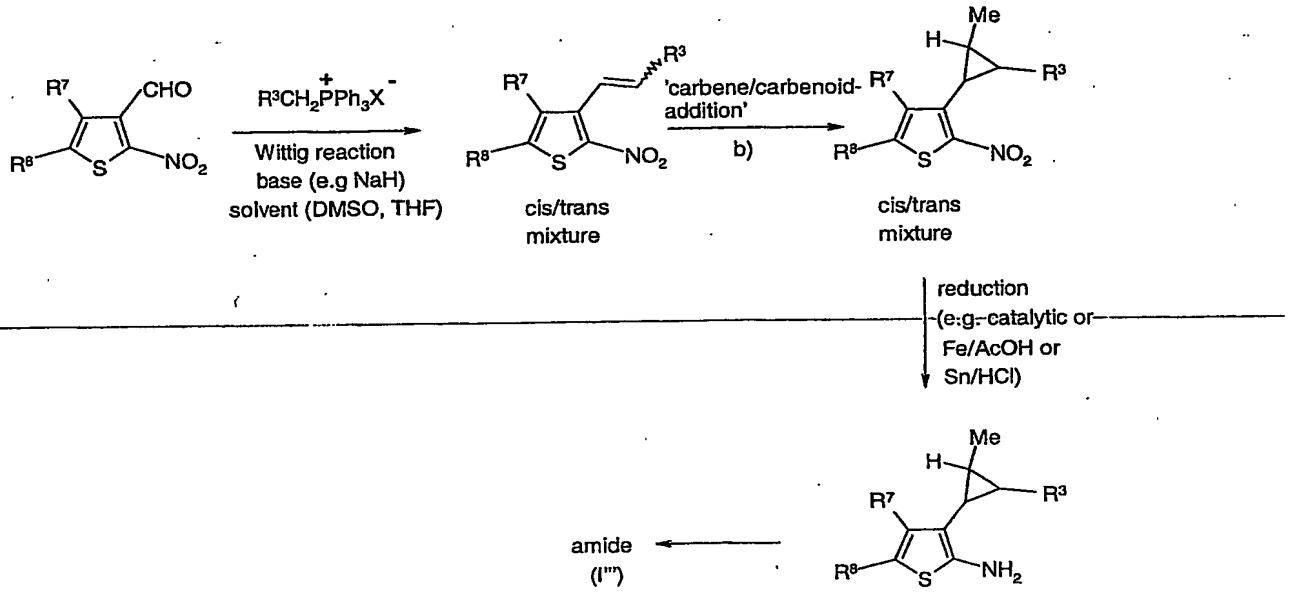
a2) (Hal = Cl): Chem.Ber. 1967, 100, 1858, Angew.Chemie 1974, 86, 744, J.Chem.Res.Synopses 1977,3, 72, Synthesis 1977, 10, 682, Patent application DE 2820410, Tertrahedron Letters 1989, 30, 4697 and Synthetic Comm. 1999, 29, 4101;

a3) (Hal = Br): Tetrahedron Letters 1973, 16, 1367, Synthetic Comm. 1973, 3, 305, J.Org.Chem. 1977, 42, 1082, J.Amer.Chem.Soc. 1985, 107, 5443 and Synthetic Comm. 1988, 18, 2117.

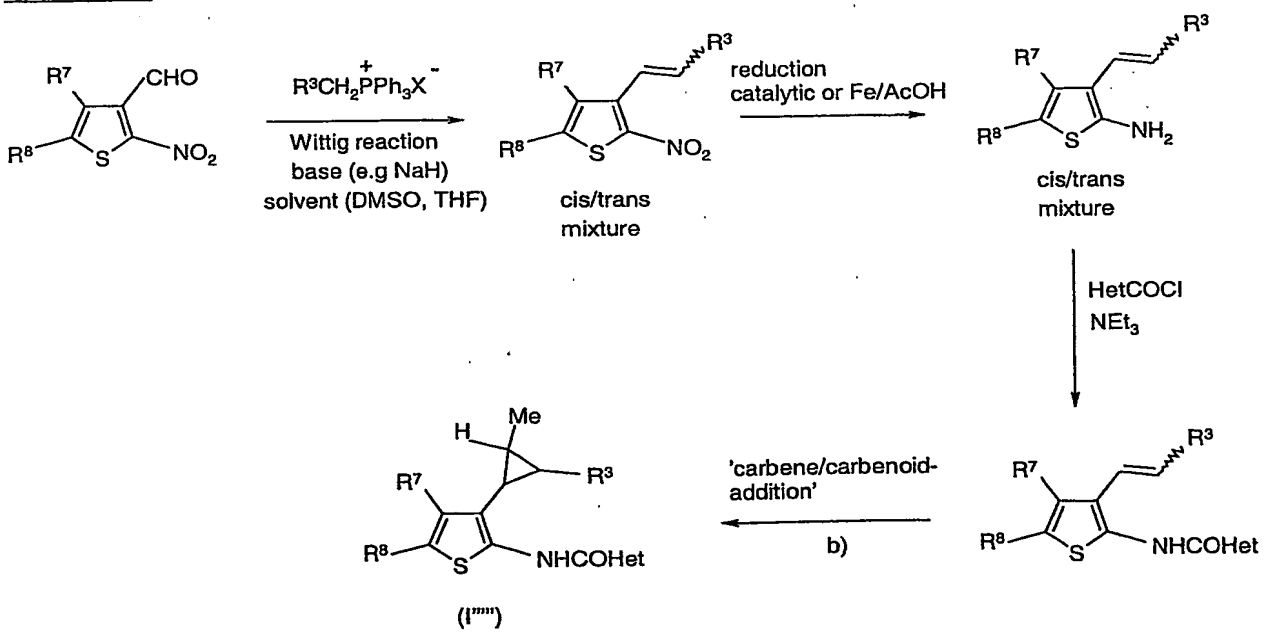
Scheme3C:



Scheme 3D:

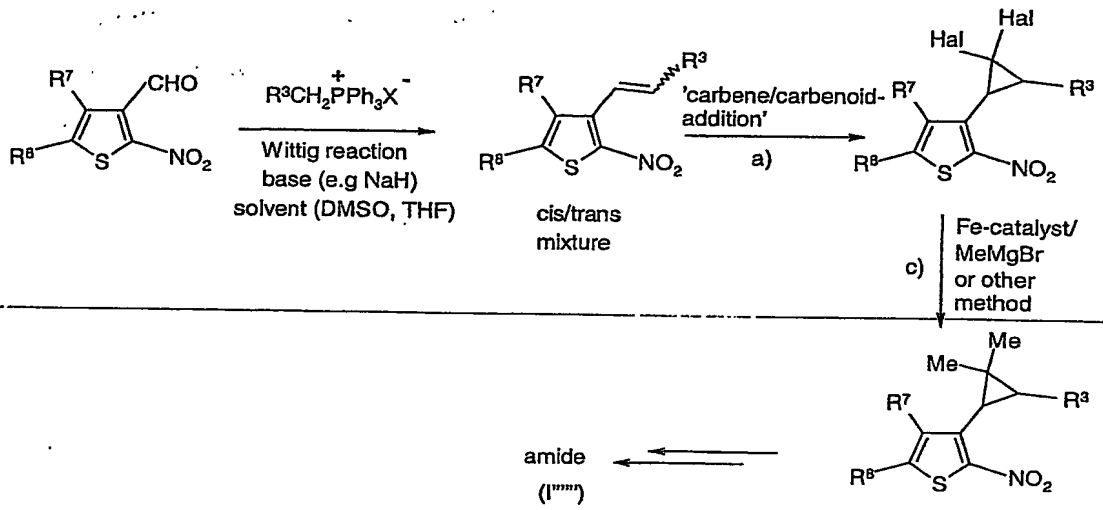


Scheme 3E:



Literature for step (b): J.Org.Chem. 1991, 56, 6974 or J.Amer.Chem.Soc. 2001, 123, 139.

Scheme 3F:



Literature for step (c): Synlett 1998, 1, 67 and Bull.Chem.Soc Jpn. 1977, 50, 1600.

In analogy to the synthesis described in schemes 3A-F, the corresponding other two thienyl isomers may be prepared using 3-nitrothiophene-2-carboxaldehyde (for example, J.Chem.Soc.Perkin Trans1 1979, 5, 1337 or Chem.Scr. 1980, 15, 135) or 3-nitrothiophene-4-carboxaldehyde (for example, Chem. Scr. 1972, 2, 245) as starting materials.

Surprisingly, it has now been found that the novel compounds of formula (I) have, for practical purposes, a very advantageous spectrum of activities for protecting plants against diseases that are caused by fungi as well as by bacteria and viruses.

The compounds of formula (I) can be used in the agricultural sector and related fields of use as active ingredients for controlling plant pests. The novel compounds are distinguished by excellent activity at low rates of application, by being well tolerated by plants and by being environmentally safe. They have very useful curative, preventive and systemic properties and are used for protecting numerous cultivated plants. The compounds of formula I can be used to inhibit or destroy the pests that occur on plants or parts of plants (fruit, blossoms, leaves, stems, tubers, roots) of different crops of useful plants, while at the same time protecting also those parts of the plants that grow later e.g. from phytopathogenic microorganisms.

It is also possible to use compounds of formula (I) as dressing agents for the treatment of plant propagation material, in particular of seeds (fruit, tubers, grains) and

plant cuttings (e.g. rice), for the protection against fungal infections as well as against phytopathogenic fungi occurring in the soil.

Furthermore the compounds according to present invention may be used for controlling fungi in related areas, for example in the protection of technical materials, including wood and wood related technical products, in food storage, in hygiene management, etc.

The compounds of formula (I) are, for example, effective against the phytopathogenic fungi of the following classes: Fungi imperfecti (e.g. Botrytis, Pyricularia, Helminthosporium, Fusarium, Septoria, Cercospora and Alternaria) and Basidiomycetes (e.g. Rhizoctonia, Hemileia, Puccinia). Additionally, they are also effective against the Ascomycetes classes (e.g. Venturia and Erysiphe, Podosphaera, Monilinia, Uncinula) and of the Oomycetes classes (e.g. Phytophthora, Pythium, Plasmopara). Outstanding activity has been observed against powdery mildew (Erysiphe spp.). Furthermore, the novel compounds of formula I are effective against phytopathogenic bacteria and viruses (e.g. against Xanthomonas spp, Pseudomonas spp, Erwinia amylovora as well as against the tobacco mosaic virus).

Within the scope of present invention, target crops to be protected typically comprise the following species of plants: cereal (wheat, barley, rye, oat, rice, maize, sorghum and related species); beet (sugar beet and fodder beet); pomes, drupes and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); leguminous plants (beans, lentils, peas, soybeans); oil plants (rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans, groundnuts); cucumber plants (pumpkins, cucumbers, melons); fibre plants (cotton, flax, hemp, jute); citrus fruit (oranges, lemons, grapefruit, mandarins); vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paprika); lauraceae (avocado, cinnamomum, camphor) or plants such as tobacco, nuts, coffee, eggplants, sugar cane, tea, pepper, vines, hops, bananas and natural rubber plants, as well as ornamentals.

The compounds of formula (I) are used in unmodified form or, preferably, together with the adjuvants conventionally employed in the art of formulation. To this end they are conveniently formulated in known manner to emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble

powders, dusts, granulates, and also encapsulations e.g. in polymeric substances. As with the type of the compositions, the methods of application, such as spraying, atomising, dusting, scattering, coating or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances. The compositions may also contain further adjuvants such as stabilizers, antifoams, viscosity regulators, binders or tackifiers as well as fertilizers, micronutrient donors or other formulations for obtaining special effects.

Suitable carriers and adjuvants can be solid or liquid and are substances useful in formulation technology, e.g. natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders or fertilizers. Such carriers are for example described in WO 97/33890.

The compounds of formula (I) are normally used in the form of compositions and can be applied to the crop area or plant to be treated, simultaneously or in succession with further compounds. These further compounds can be e.g. fertilizers or micronutrient donors or other preparations which influence the growth of plants. They can also be selective herbicides as well as insecticides, fungicides, bactericides, nematicides, molluscicides or mixtures of several of these preparations, if desired together with further carriers, surfactants or application promoting adjuvants customarily employed in the art of formulation.

The compounds of formula (I) can be mixed with other fungicides, resulting in some cases in unexpected synergistic activities. Mixing components which are particularly preferred are azoles, such as azaconazole, BAY 14120, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, imibenconazole, ipconazole, metconazole, myclobutanil, pefurazoate, penconazole, pyrifenox, prochloraz, propiconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole, triticonazole; pyrimidinyl carbinole, such as ancymidol, fenarimol, nuarimol; 2-amino-pyrimidines, such as bupirimate, dimethirimol, ethirimol; morpholines, such as dodemorph, fenpropidine, fenpropimorph, spiroxamine, tridemorph; anilinopyrimidines, such as cyprodinil, mepanipyrim, pyrimethanil; pyrroles, such as fenpiclonil, fludioxonil; phenylamides, such as benalaxyl, furalaxyl, metalaxyl, R-metalaxyl, ofurace, oxadixyl; benzimidazoles, such as benomyl, carbendazim, debacarb, fuberidazole, thiabendazole;

dicarboximides, such as chlozolinate, dichlozoline, iprodione, myclozoline, procymidone, vinclozoline; carboxamides, such as carboxin, fenfuram, flutolanil, mepronil, oxycarboxin, thifluzamide; guanidines, such as guazatine, dodine, iminoctadine; strobilurines, such as azoxystrobin, kresoxim-methyl, metominostrobin, SSF-129, trifloxystrobin, picoxystrobin, BAS 500F (proposed name pyraclostrobin), BAS 520; dithiocarbamates, such as ferbam, mancozeb, maneb, metiram, propineb, thiram, zineb, ziram; N-halomethylthiotetrahydro-phthalimides, such as captafol, captan, dichlofluanid, fluoromides, folpet, tolyfluanid; Cu-compounds, such as Bordeaux mixture, copper hydroxide, copper oxychloride, copper sulfate, cuprous oxide, mancopper, oxine-copper; nitrophenol-derivatives, such as dinocap, nitrothal-isopropyl; organo-p-derivatives, such as edifenphos, iprobenphos, isoprothiolane, phosdiphen, pyrazophos, tolclofos-methyl; various others, such as acibenzolar-S-methyl, anilazine, benthiavalicarb, blasticidin-S, chinomethionate, chloroneb, chlorothalonil, cyflufenamid, cymoxanil, dichlone, diclomezine, dicloran, diethofencarb, dimethomorph, SYP-LI90 (proposed name: flumorph), dithianon, ethaboxam, etridiazole, famoxadone, fenamidone, fenoxanil, fentin, ferimzone, fluazinam, flusulfamide, fenhexamid, fosetyl-aluminium, hymexazol, iprovalicarb, IKF-916 (cyazofamid), kasugamycin, methasulfocarb, metrafenone, nicobifen, pencycuron, phthalide, polyoxins, probenazole, propamocarb, pyroquilon, quinoxyfen, quintozene, sulfur, triazoxide, tricyclazole, triforine, validamycin, zoxamide (RH7281).

A preferred method of applying a compound of formula (I), or an agrochemical composition which contains at least one of said compounds, is foliar application. The frequency of application and the rate of application will depend on the risk of infestation by the corresponding pathogen. However, the compounds of formula I can also penetrate the plant through the roots via the soil (systemic action) by drenching the locus of the plant with a liquid formulation, or by applying the compounds in solid form to the soil, e.g. in granular form (soil application). In crops of water rice such granulates can be applied to the flooded rice field. The compounds of formula I may also be applied to seeds (coating) by impregnating the seeds or tubers either with a liquid formulation of the fungicide or coating them with a solid formulation.

A formulation [that is, a composition containing the compound of formula (I)] and, if desired, a solid or liquid adjuvant, is prepared in a known manner, typically by intimately

mixing and/or grinding the compound with extenders, for example solvents, solid carriers and, optionally, surface active compounds (surfactants).

The agrochemical formulations will usually contain from 0.1 to 99% by weight, preferably from 0.1 to 95% by weight, of the compound of formula I, 99.9 to 1% by weight, preferably 99.8 to 5% by weight, of a solid or liquid adjuvant, and from 0 to 25% by weight, preferably from 0.1 to 25% by weight, of a surfactant.

Advantageous rates of application are normally from 5g to 2kg of active ingredient (a.i.) per hectare (ha), preferably from 10g to 1kg a.i./ha, most preferably from 20g to 600g a.i./ha. When used as seed drenching agent, convenient dosages are from 10mg to 1g of active substance per kg of seeds.

Whereas it is preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations.

The following non-limiting Examples illustrate the above-described invention in more detail.

EXAMPLE 1

This Example illustrates the preparation of Compound 1.10.

In a sulfonation flask, 0.37g (0.02mol) of NaH (55%) was added to 50ml of absolute DMSO. After heating at 80°C for 90minutes, 8.5g (0.02mol) cyclopropylcarbonylmethyl-triphenylphosphonium bromide was added portionwise. The resulting suspension was stirred for 45minutes at room temperature and then a solution of 3.82g (0.02mol) 3-bromo-2-formylthiophene in 15ml DMSO was added dropwise. After heating the resulting mixture for 3hours at 50°C, the mixture was poured onto 300ml of ice water. Extraction with ethylacetate, drying over Na_2SO_4 and distilling off the solvent in a water jet vacuum yielded the crude product. Purification was achieved by distillation.

Yield: 4.45g E-3-(3-bromothiophen-2-yl)-1-cyclo-propylpropenone as a yellow oil (b.p.: 95°C at 1Pa).

In a sulfonation flask, a mixture of 4.23g (16mmol) E-3-(3-bromothiophenyl-2-yl)-1-cyclopropylpropenone and 1.2g (23.4mmol) hyrazine hydrate in 25ml of ethanol was heated at reflux temperature for 2hours. Then 1.27g (19.2mmol) powdered potassium hydroxide (85%) was added and any excesses of hydrazine and solvent were distilled out of the flask. The remaining mixture was then heated at a temperature of 185-190°C for

1hour. The resulting resin was dissolved in 75ml ethylacetate at a temperature of ca.50°C. After washing with water, drying off the ethylacetate phase over Na_2SO_4 and destilling off the solvent in a water jet vacuum, the crude product was obtained. Purification was achieved by using flash-chromatography over silica gel (eluant: hexane/ethylacetate 30:1). Yield: 1.53g of 2-bicyclo-propyl-2-yl-3-bromothiophene in the form of a colourless oil (cis/trans-mixture).

A mixture of 1.37g (5.63mmol) of 2-bicyclopropyl-2-yl-3-bromothiophene, 1.22g (6.75mmol) benzophenonimine, 0.76g (7.88mmol) sodium tert-butoxide, 0.0021g (0.022mmol) tris-dibenzylidenacetondipalladium ($Pd_2(dba)_3$), 0.039g (0.063mmol) rac.-2,2'-bis(diphenylphosphino)1,1-binaphthyl (BINAP) and 40ml of absolute toluene was heated at reflux temperature under an atmosphere of nitrogene for 15hours. After cooling, the reaction mixture was diluted with 200ml of acetylacetate and the organic layer was washed several times with brine. After drying the organic phase (Na_2SO_4) and evaporation of the solvent, the crude product was obtained. The raw material was purified by flash chromatography over silica gel (eluant: hexane/diisopropylether 20:1). Yield: 1.85g benzhydrilidene-(2-bicyclo-propyl-2-yl-thiophen-3-yl)amine in the form of a yellow oil.

In a sulfonation flask, 0.61g (8.7mmol) hydroxylamine hydrochloride and 0.95g (11.62mmol) sodiumacetate and 40ml methanol were stirred for ca.30minutes. Then a solution 1.66g (4.84mmol) benzhydrilidene-(2-bicyclopropyl-2-yl-thiophen-3-yl)amine in 10ml methanol was added dropwise. Stirring at room temperature continued for 2hours. The reaction mixture was poured onto 300ml of ice water. Extraction with ethylacetate, drying of the organic phase (Na_2SO_4) and evaporation of the solvent gave the raw material. The crude product was purified by flash-chromatography over silica gel (eluant: hexane/diisopropylether 2:1). Yield: 0.78g 2-bicyclopropyl-2-ylthiophen-3-ylamine in the form of an orange oil (cis/trans-mixture; ratio ca. 1:5.5). The trans isomer was separated in pure form after an additional flash-chromatographic purification.

EXAMPLE 2

This Example illustrates the preparation of Compound 4.34.

To a solution consisting of 0.210g (1.12mmol) 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid, 0.185g (1.03mol) 2-bicyclopropyl-2-yl-thiophen-3-ylamine, 0.21g (2.05mmol) triethylamine and 5ml methylenechloride was added 0.3g (1.18mmol)

of N,N-bis(2-oxo-oxazolidinyl)phosphinic acid chloride (BOP-Cl) at 0°C. Then the ice bath was removed and the mixture was stirred at room temperature for 15hours. Then the solvent was removed and the residue was directly purified by flash-chromatography over silica gel (eluant: hexane/ethylacetate 3:2). The resin so obtained was crystallised in cold pentane yielding the trans isomer in a purity of 97%. Yield: 0.21g of 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (2-bicyclo-propyl-2-yl-thiophen-3-yl)amide in the form of a white powder (trans-isomer with a purity of 97%); m.p.:76-79°C.

FORMULATION EXAMPLES FOR COMPOUNDS OF FORMULA (I)

Working procedures for preparing formulations of the compounds of formula (I), such as Emulsifiable Concentrates, Solutions, Granules, Dusts and Wettable Powders are described in WO 97/33890.

Biological Examples: Fungicidal actions

Example B-1: Action against Puccinia recondita / wheat (Brownrust on wheat)

1 week old wheat plants cv. Arina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application wheat plants are inoculated by spraying a spore suspension ($1x10^5$uredospores/ml) on the test plants. After an incubation period of 2 days at 20°C and 95%r.h. plants are kept in a greenhouse for 8days at 20°C and 60%r.h. The disease incidence is assessed 10days after inoculation.

Compounds of Tables 4-12 show good activity in this test (<20% infestation). Infestation is prevented virtually completely (0-5% infestation) with each of compounds 4.23, 4.24, 4.33, 4.34, 4.77, 4.78, 5.23, 5.33, 5.76, 10.12, 10.20 and 10.49.

Example B-2: Action against Podosphaera leucotricha / apple (Powdery mildew on apple)

5 week old apple seedlings cv. McIntosh are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. One day after application apple plants are inoculated by shaking plants infected with apple powdery mildew above the test plants. After an incubation period of 12days at 22°C and 60%r.h. under a light regime of 14/10hours (light/dark) the disease incidence is assessed.

Compounds of Tables 4, 5 and 10 show good activity in this test. Compounds 4.23, 4.24, 4.33, 4.34, 4.76, 4.77, 4.78, 5.23, 5.33, 5.76, 10.12, 10.20 and 10.49 each exhibit strong efficacy (<20% infestation).

Example B-3: Action against Venturia inaequalis / apple (Scab on apple)

4 week old apple seedlings cv. McIntosh are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application apple plants are inoculated by spraying a spore suspension ($4x10^5$conidia/ml) on the test plants. After an incubation period of 4days at 21°C and 95%r.h. the plants are placed for 4days at 21°C and 60%r.h. in a greenhouse. After another 4day incubation period at 21°C and 95%r.h. the disease incidence is assessed.

Compounds of Tables 4, 5 and 10 show good activity in this test. Compounds 4.23, 4.24, 4.33, 4.34, 4.76, 4.77, 4.78, 5.23, 5.33, 5.76, 10.12, 10.20 and 10.49 each exhibit strong efficacy (<20% infestation).

Example B-4: Action against Erysiphe graminis / barley (Powdery mildew on barley)

1 week old barley plants cv. Express are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application barley plants are inoculated by shaking powdery mildew infected plants above the test plants. After an incubation period of 6 days at 20°C / 18°C (day/night) and 60%r.h. in a greenhouse the disease incidence is assessed.

Compounds of Tables 4, 5 and 10 show good activity in this test. Compounds 4.23, 4.24, 4.33, 4.34, 4.76, 4.77, 4.78, 5.23, 5.33, 5.76, 10.12, 10.20 and 10.49 each exhibit strong efficacy (<20% infestation).

Example B-5: Action against Pyrenophora teres / barley (Net blotch on barley)

1 week old barley plants cv. Express are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. Two days after application barley plants are inoculated by spraying a spore suspension ($3x10^4$conidia/ml) on the test plants. After an incubation period of 2 days at 20°C and 95%r.h. plants are kept for 2 days at 20°C and 60%r.h. in a greenhouse. The disease incidence is assessed 4 days after inoculation.

Compounds of Tables 4-18 show good activity in this test. Compounds 4.23, 4.24, 4.33, 4.34, 4.76, 4.77, 4.78, 5.23, 5.33, 5.76, 10.12, 10.20, 10.49, 13.11 and 13.53 each exhibit strong efficacy (<20% infestation).

Example B-6: Action against Alternaria solani / tomato (Early blight on tomatoes)

4 week old tomato plants cv. Roter Gnom are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. Two days after application, the tomato plants are inoculated by spraying a spore suspension ($2x10^5$conidia/ml) on the test

plants. After an incubation period of 3 days at 20°C and 95%r.h. in a growth chamber the disease incidence is assessed.

Compounds 4.33, 4.34, 4.76, 4.77, 4.78, 5.33, 5.76, 10.20, 10.49 and 13.53 each show good activity in this test (<20% disease incidence).

Example B-7: Action against Uncinula necator / grape (Powdery mildew on grapes)

5 week old grape seedlings cv. Gutedel are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application, the grape plants are inoculated by shaking plants infected with grape powdery mildew above the test plants. After an incubation period of 7 days at 26°C and 60%r.h. under a light regime of 14/10hours (light/dark) the disease incidence is assessed.

Compounds 4.33, 4.34, 4.76, 4.77, 4.78, 5.33, 5.76, 10.20 and 13.53 each show good activity in this test (<20% disease incidence).

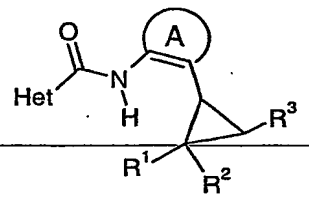
Example B-8: Action against Septoria tritici / wheat (Septoria leaf spot on wheat)

2 week old wheat plants cv. Riband are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application, wheat plants are inoculated by spraying a spore suspension ($10x10^5$conidia/ml) on the test plants. After an incubation period of 1 day at 23°C and 95% r.h., the plants are kept for 16 days at 23°C and 60%r.h. in a greenhouse. The disease incidence is assessed 18 days after inoculation.

Compounds 4.76, 4.77, 4.78, 5.76 and 10.49 each show good activity in this test (<20% disease incidence).

CLAIMS

1. A compound of formula (I):



(I)

where

Het is a 5- or 6-membered heterocyclic ring containing one to three heteroatoms, each independently selected from oxygen, nitrogen and sulphur, provided that the ring is not 1,2,3-triazole, the ring being substituted by groups R^4, R^5 and R^6;

A is a thienyl ring (selected from all possible thienyl isomers) being substituted by groups R^7 and R^8;

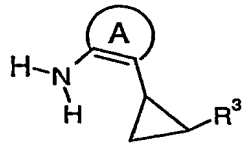
R^1 and R^2 are each, independently, hydrogen, halo or methyl;

R^3 is optionally substituted C_{2-12} alkyl, optionally substituted C_{2-12} alkenyl, optionally substituted C_{2-12} alkynyl, optionally substituted C_{3-12} cycloalkyl, optionally substituted phenyl or optionally substituted heterocyclyl;

R^4, R^5 and R^6 are each, independently, selected from hydrogen, halo, cyano, nitro, C_{1-4} alkyl, C_{1-4} haloalkyl, C_{1-4} alkoxy(C_{1-4})alkylene and C_{1-4} haloalkoxy(C_{1-4})alkylene, provided that at least one of R^4, R^5 and R^6 is not hydrogen; and

R^7 and R^8 are each, independently, hydrogen, halogen, C_{1-4}alkyl or C_{1-4}haloalkyl.

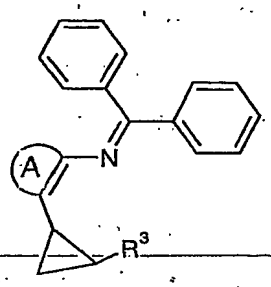
2. A compound of formula (II):



(II)

where A is an unsubstituted thienyl ring (selected from all possible thienyl isomers) and R^3 is as defined in claim 1.

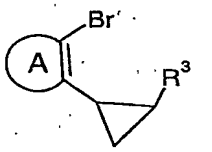
3. A process for preparing a compound of formula (II) as claimed in claim 2 from a compound of formula (V)



(V)

where A is an unsubstituted thienyl ring (selected from all possible thienyl isomers) and R^3 is as defined above for a compound of formula (I), comprising either a transamination reaction of a compound of formula (V) with hydroxylamine hydrochloride in the presence of a base or a hydrolysis reaction of a compound of formula (V) with an acid.

4. A process for preparing a compound of formula (V) as defined in claim 3 from a compound of formula (IV)



(IV)

where A is a thienyl ring (selected from all possible thienyl isomers) and R^3 is as defined above for a compound of formula (I), comprising tris-dibenzylidenacetondipalladium-catalysed reaction of a compound of formula (IV) with benzophenonimine in the presence of a strong base and a ligand in a solvent at temperatures of 30°C up to reflux temperature.

5. A composition for controlling microorganisms and preventing attack and infestation of plants therewith, wherein the active ingredient is a compound of formula (I) as claimed in claim 1 together with a suitable carrier.

6. A method of controlling or preventing infestation of cultivated plants by phytopathogenic microorganisms by application of a compound of formula (I) as claimed in claim 1 to plants, to parts thereof or the locus thereof.